

PATENT SPECIFICATION

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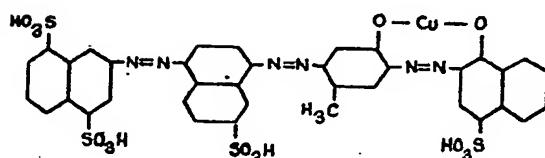
COMPLETE SPECIFICATION

Metalliferous Trisazo-Dyestuffs and process for making them

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides new metalliferous trisazo-dyestuffs which, as for example in the case of the complex compound of the formula

(1)



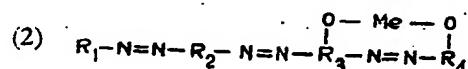
correspond to the general formula

(3) $R_1-N=N-R_2-N=N-R_3-N=N-R_4$

in which R_1 represents the residue of an initial component free from hydroxyl groups, R_2 represents an aromatic residue containing at most 10 aryl carbon atoms, R_3 represents an aromatic residue of the benzene series, and

R_4 represents a residue of an oxynaphthalene sulphonic acid free from amino groups and bound to the azo-linkage in a position vicinal to a hydroxyl group or represents a 5-pyrazolone residue, and in which the azo linkages connected to the residues R_2 and R_3 are bound in para-position relatively to one another, and the residue R_3 contains an alkoxy group of low molecular weight in a position vicinal to the azo linkage connecting R_3 with R_4 , with an agent yielding copper or nickel under conditions such that the corresponding ortho: ortho'-dioxy-azo-metal complex is formed.

(Price Billed) Rs 6d



in which the group $-O-Me-O$ is bound to the residues R_3 and R_4 in positions vicinal to the azo linkage, Me represents the metal copper or nickel, R_1 represents the residue of an initial component free from hydroxyl groups, R_2 represents an aromatic residue containing at most 10 aryl carbon atoms, R_3 represents an aromatic residue of the benzene series, and R_4 represents a naphthalene residue free from amino groups and containing at least one sulphonic acid group or represents a 5-pyrazolone residue, and in which the azo linkages connected to the residues R_2 and R_3 are bound in para-position relatively to one another.

The metalliferous azo-dyestuffs of the general formula (2) are made in accordance with the invention by treating a trisazo-dyestuff corresponding to the general formula

The trisazo-dyestuffs of the formula (3) serving as starting materials may be prepared by coupling a diazotised initial component free from hydroxyl groups with a middle component of the benzene or naphthalene series, that is to say, with an aminobenzene or aminonaphthalene capable of coupling in para-position relatively to the amino group, then diazotising the amino-monoazo-dyestuff, and coupling the diazo compound with a middle component of the benzene series which contains an alkoxy group of low molecular weight in a position vicinal to the amino group, converting the resulting amino-disazo-dyestuff into its diazo compound, and finally coupling the latter either with an oxynaphthalene sulphonic acid free from amino groups or with a 5-pyrazolone.

As initial components, from which the dyestuffs of the formula (3) are to be prepared

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by the method described above, there come into consideration, for example, aryl amines of the benzene or naphthalene series or those having more than two fused 6-membered rings which arylamines are free from hydroxyl groups, but may be otherwise substituted in any desired manner, and advantageously contain sulphonate acid groups. As examples there may be mentioned amino-benzene sulphonate acids such as 1-aminobenzene-3- or -4-sulphonate acid, aminobenzene-2:5-disulphonate acid, aminonaphthalene sulphonate acids such as 1-aminonaphthalene-4- or -5-sulphonate acid, 1-amino-4-nitronaphthalene-5-sulphonate acid, 1-aminonaphthalene-5:7-disulphonate acid, 2-aminonaphthalene-4:8- or -5:7-disulphonate acid or 2-aminopyrene disulphonate acid, and also amines which contain two non-fused 6-membered rings such as 4-amino-4¹-acetylaminio-1:1¹-diphenyl-3-sulphonate acid, or initial components containing heterocyclic rings such as 2-(4¹-amino-phenyl)-6-methyl-benzothiazole sulphonate acid.

The first middle component, which yields the residue R₂ in the dyestuffs of the formula (3), may be of the benzene series, for example, aminobenzene, 1-amino-2- or -3-methyl-benzene or 1-amino-2:5-dimethylbenzene. In some cases it is especially advantageous to use middle components of the naphthalene series such as 1-aminonaphthalene, 1-aminonaphthalene-6- or -7-sulphonate acid or the commercial mixture of these two acids.

The second middle component yielding the residue R₃ must be one of the benzene series and must also contain in a position vicinal to the amino group an alkoxy group of low molecular weight, that is to say, one which contains only few carbon atoms such, for example, as an ethoxy group or advantageously a methoxy group. As examples of such middle components there may be mentioned more especially amino-ortho-methoxybenzenes such as 1-amino-2-methoxybenzene, 1-amino-2-methoxy-5-methylbenzene, 1-amino-2:5-dimethoxybenzene, and also 1-amino-2-ethoxy-5-methyl benzene.

As end components for making the trisazo-dyestuffs there come into consideration advantageously oxynaphthalene sulphonate acids capable of coupling in a position vicinal to a hydroxyl group. These components may contain one or 2 or, if desired, even 3 sulphonate acid groups and may contain further substituents, with the exception of free or substituted amino groups, such as an additional hydroxyl group, a halogen atom especially chlorine, or an alkoxy group. As examples there may be mentioned 1-oxynaphthalene-4-sulphonate acid, 2-oxynaphthalene-4- or -6- or -7-sulphonate acid, 1-oxynaphthalene-3:6- or -3:8- or -4:8-disulphonate acid, 2-oxynaphthalene-3:6- or -6:8-disulphonate acid and 1:8-dioxynaphthalene-3:6-disulphonate acid.

Instead of oxynaphthalene sulphonate acids there may be used as end components 5-pyrazolones such as 3-methyl-5-pyrazolone, 1-phenyl-3-methyl-5-pyrazolone-3-sulphonate acid or -3-sulphonate acid amide or 1-phenyl-5-pyrazolone-3-carboxylic acid.

It is of advantage so to choose the starting materials that the resulting trisazo-dyestuff contains at least three and at most six, and advantageously three to four, sulphonate acid groups. When only a few sulphonate acid groups are present, and the solubility in water of the metalliferous dyestuffs obtainable therefrom in accordance with the present process is insufficient, the solubility can in general be substantially improved by the presence of other groups imparting solubility such as carboxylic acid groups or sulphonate acid amide groups.

The reactions necessary for making the trisazo-dyestuffs used as starting materials in the present process, that is to say, the diazotisations and couplings, may be carried out by the usual known methods. Couplings with the middle components are usually carried out with advantage in a weakly acid medium. Middle components having a low capacity for coupling such as aminobenzene, 2-methyl- or 2-methoxy-1-aminobenzene are advantageously coupled in the form of their ω -methane sulphonate acids, and the ω -methane sulphonate acid residues is subsequently split off. For the final coupling with the oxynaphthalene sulphonate acids it is of advantage to work in an alkaline medium, for example, a medium rendered alkaline with an alkali carbonate, and, if desired, to accelerate the reaction by suitable additions such as alcohol or especially pyridine.

As a rule it is of advantage to separate the trisazo-dyestuff from the coupling mixture before carrying out the metallisation, and then to metallise the dyestuff without any intermediate drying. In some cases, however, it is unnecessary to isolate the dyestuff from the coupling mixture.

As agents yielding metal there are used in the present process agents yielding nickel or advantageously those yielding copper. There may be used, for example, salts of divalent nickel such as nickel (Ni . .) sulphate, salts of mono- or divalent copper, such as cuprous chloride or cupric sulphate, and also compounds which contain these metals in complex union. In the latter connection there are especially suitable nickel- or copper-ammine complexes such, for example, as the complex nickel or copper compounds obtainable from ammonia, alkylamines such as ethylamine, morpholine, pyridine, picolines or piperidine. In order to ensure the complete splitting off of the alkyl groups from the alkoxy groups with the formation of a metal complex of the trisazo-

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5 dyestuff it is usually necessary to carry out the treatment with the agent yielding metal at a raised temperature, for example, at about 90° C. and for several hours. It is also of advantage to work in an aqueous medium. If desired, the treatment with the agent yielding metal may be carried out in the presence of suitable additions. As such additions there may be mentioned, bases such as ammonia or 10 pyridine, for example, an excess of the base which is present in the molecule of the metal ammine complex when such is used as an agent yielding metal.

15 In some cases very good results are obtained by carrying out the treatment with the agent yielding metal in the presence of an ethanolamine. Such treatment is in accordance with Specification No. 644,883 which describes and claims a process for the manufacture of metalliferous azo-dyestuffs, wherein an ortho-alkoxy-ortho'-oxy-azo-dyestuff, which contains at least one sulphonate acid group and at least two azo-groups, is treated 20 in the presence of an aliphatic amine containing a hydroxyl group, for example, an ethanolamine, with an agent yielding metal until the alkoxy group or groups is or are split up.

25 The metalliferous dyestuffs of the invention are new and correspond to the formula (2) given above. The latter formula undoubtedly represents the correct stoichiometric proportions of nickel or copper and the correct position of the metal atom in the complex. However, the distribution of main and secondary valencies in the complex union of the metal has not been established with certainty.

30 These trisazo-dyestuffs produced from simple components are suitable for dyeing or printing a very wide variety of materials for example, those of animal origin such as wool or leather. Owing to their good affinity for vegetable fibres they are especially suitable for dyeing or printing cellulose-containing materials such as linen, cotton and artificial silk or staple fibres of regenerated cellulose. They possess good levelling properties, which is also of advantage for dyeing streaky artificial silk from viscose. The dyeings obtainable with the new metalliferous dyestuffs on cellulose fibres are usually distinguished by their very desirable grey tints and also by their good properties of wet fastness and above all by their very good fastness to light. Even in the case of weak dyeings the fastness to light is surprising, and generally speaking the fastness to light is not diminished to any important extent by the usual treatments used to impart anti-creasing properties.

35 The following Examples illustrate the invention the parts and percentages being by weight unless otherwise stated and the relationship of parts by weight to parts by volume being the same as that of the kilogram to the

litre:

EXAMPLE 1.

40 7.5 parts of the sodium salt of the disazo-dyestuff obtained by coupling diazotised 2-aminonaphthalene-4:8-disulphonic acid with 70 1-aminonaphthalene-7-sulphonic acid, further diazotising and then coupling with 1-amino-2-methoxy-5-methylbenzene, are dissolved in 100 parts of warm water, cooled with ice to 15-20° C., and diazotised by the addition of 0.7 part of sodium nitrite dissolved in 5 parts of water and pouring in 3.5 parts of hydrochloric acid of 30 per cent. strength which has been diluted with about 6 parts of water. The mixture is stirred for about 2 hours at 10-15° C., and the diazo compound is then coupled with a solution, rendered alkaline with sodium carbonate, of 2.3 parts of 1-oxynaphthalene-4-sulphonic acid. The coupling may be accelerated by the addition of a small amount of pyridine. When the diazo compound can no longer be detected, there are added approximately 10 parts of sodium chloride for every 10 parts by volume of the coupling mixture, and the dyestuff is 45 filtered off. In order to convert the dyestuff into its complex copper compound, the dyestuff is dissolved in 300 parts of hot water, 100 parts of pyridine are added, followed by a copper solution consisting of 3 parts of crystalline copper sulphate, 12 parts of water and 4.8 parts by volume of ammonia solution of 30 per cent. strength. The whole is stirred for about 6 hours at 90-95° C., the pyridine is 50 distilled off in vacuo, and the dyestuff is precipitated by the addition of sodium chloride. When dry, the dyestuff is a blackish powder which dissolves in water with a grey-blue coloration and in concentrated sulphuric acid with a reddish blue coloration, and dyes cotton grey tints which are fast to light.

EXAMPLE 2.

55 The amino-disazo-dyestuff used in Example 1 is diazotised as described in that Example and coupled in a solution rendered alkaline with sodium carbonate, and advantageously with the addition of a small amount of pyridine, with 3.2 parts of 1-oxynaphthalene-4:8-disulphonic acid. When the coupling has finished there are added about 5 parts of sodium chloride for every 100 parts by volume of the mixture, and the dyestuff is 60 filtered off. The dyestuff is dissolved in 200 parts of hot water and 40 parts of pyridine, and, after the addition of a copper solution consisting of 3 parts of crystalline copper sulphate, 12 parts of water and 4.8 parts by volume of ammonia solution of 30 per cent. strength, the whole is stirred for 6 hours at 90-95° C. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 65 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 70 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 75 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 80 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 85 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 90 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 95 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 100 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 105 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 110 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 115 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 120 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 125 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration. The pyridine is then distilled off in vacuo and the dyestuff is precipitated by the addition of about 30 parts of sodium chloride. The dyestuff when dry is a blackish powder which dissolves in water with a 130 greenish blue coloration and in concentrated sulphuric acid with a reddish blue coloration.

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sulphuric acid with a reddish blue coloration, and dyes cotton grey tints which are fast to light.

5 A dyestuff which dyes somewhat more greenish shades of similar fastness to light is produced by using 1-oxynaphthalene-3:8-disulphonic acid as end component.

10 The dyestuff obtained by using 2-oxynaphthalene-4-sulphonic acid yields an olive-grey tint.

EXAMPLE 3.

15 6.5 parts of the sodium salt of the disazo-dyestuff, which is obtained by coupling diazo-tised-2-aminonaphthalene - 4:8 - disulphonic acid with 1-aminonaphthalene, further diazo-tising and then coupling with 1-amino-2-methoxy-5-methyl-benzene, are dissolved in 100 parts of warm water, then cooled with ice to 18-20° C., and diazotised by the addition 20 of 0.7 part of sodium nitrite dissolved in 5 parts of water and by pouring in 3 parts of hydrochloric acid of 30 per cent. strength which has been diluted with about 6 parts of water. Stirring is continued until non-diazo-tised dyestuff can no longer be detected, and 25 coupling is then carried out at 0-5° C. with 3.2 parts of 1-oxynaphthalene - 3:8 - disulphonic acid in a solution rendered alkaline with sodium carbonate, and advantageously 30 in the presence of a small amount of pyridine. When the diazo compound can no longer be detected, about 10 parts of sodium chloride are added for every 100 parts by volume of the coupling mixture, and the dyestuff is filtered off. In order to convert the dyestuff into its 35 complex copper compound it is dissolved in 300 parts of hot water, 60 parts of pyridine are added and then a copper solution consisting of 3 parts of crystalline copper sulphate, 12 parts of water and 4.8 parts by volume of ammonia solution of 30 per cent. strength. The whole is stirred for about 6 hours at 90-95° C. and the dyestuff is precipitated by the addition of 300 parts of 40 sodium chloride solution of 30 per cent. strength. The dry dyestuff is a blackish powder which dissolves in water with a blue coloration and in concentrated sulphuric acid with a dull blue coloration, and dyes cotton 45 level blue-grey tints which are fast to light.

50 The coppering may also be carried out in the absence of pyridine, if desired in the presence of a small quantity of ethanolamine.

55 A valuable dyestuff is also obtained by using, instead of copper sulphate, an equivalent quantity of nickel sulphate.

EXAMPLE 4.

60 6.5 parts of the sodium salt of the disazo-dyestuff, which is obtained by coupling diazo-tised-2-aminonaphthalene - 5:7 - disulphonic acid with 1-aminonaphthalene, further diazo-tising and then coupling with 1-amino-2-methoxy-5-methylbenzene, are diazotised as described in Example 1. The resulting 65 thickly liquid diazo-magma is coupled with

3.2 parts of 1-oxynaphthalene - 4:8 - disulphonic acid in the presence of a small amount of pyridine in a solution rendered alkaline with sodium carbonate at 0-5° C. When the coupling is finished the precipitated dyestuff is filtered off. It is dissolved in 200 parts of hot water and 40 parts of pyridine and converted into its copper compound as described in Example 1. The precipitated and dried dyestuff is a blackish powder which dissolves in water with a blue coloration and in concentrated sulphuric acid with a dull violet coloration. On cotton it yields level grey dyeings of good fastness to light.

EXAMPLE 5.

70 7.7 parts of the sodium salt of the disazo-dyestuff, which is obtained by coupling diazo-tised 2-aminonaphthalene-4:8-disulphonic acid with 1-aminonaphthalene-7-sulphonic acid, further diazotising and then coupling with 1-amino-2:5-dimethoxybenzene, are dissolved in 100 parts of water and diazotised at about 20° C. after the addition of 0.7 part of sodium nitrite dissolved in 5 parts of water and 3 parts of hydrochloric acid of 30 per cent. strength diluted with a small amount of water. The whole is stirred for a few hours and then coupled at 0-5° C. with 2.3 parts of 1-oxy-naphthalene-4-sulphonic acid in a solution rendered alkaline with sodium carbonate, and advantageously in the presence of a small amount of pyridine. After a few hours, when the dyestuff has precipitated sufficiently, it is filtered off. It is dissolved in 200 parts of hot water and 40 parts of pyridine and converted into its copper compound as described in Example 1. The copper compound in the dry state is a blackish powder which dissolves in water with a green-blue coloration and in concentrated sulphuric acid with a dull blue coloration, and dyes cotton very level blackish grey tints which are fast to light.

75 A dyestuff having similar properties is obtained by coupling the diazo disazo-compound with 1-phenyl-3-methyl-5-pyrazolone-3'-sulphonic acid amide instead of 1-oxynaphthalene-4-sulphonic acid.

EXAMPLE 6.

80 6 parts of the sodium salt of the disazo-dyestuff, which is obtained by coupling diazo-tised 1-aminobenzene-4-sulphonic acid with 1-aminonaphthalene-7-sulphonic acid, further diazotising and then coupling with 1-amino-2-methoxy-5-methylbenzene, are diazotised as described in Example 1 and then coupled to 0-5° C. with 2.3 parts of 1-oxynaphthalene-4-sulphonic acid in a solution rendered alkaline with sodium carbonate. The coupling may be accelerated by the addition of a small amount of pyridine. The dyestuff is precipitated by the addition of 10-15 parts of sodium chloride for every 100 parts by volume of coupling mixture, and the dyestuff is filtered off. It is dissolved in 100 parts of hot

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water and 40 parts of pyridine, and converted into its copper compound as described in Example 1. The drye dyestuff is a blackish powder which dissolves in water and in concentrated sulphuric acid with a dull reddish blue coloration. It yields on cotton very level grey tints which are fast to light.

By using 1-aminobenzene-3-sulphonic acid as initial component a very similar dyestuff

is obtained

In the following Table are given a few further cupriferous trisazo-dyestuffs which can be made in the manner described in the foregoing Examples by coppering accompanied by de-alkylation trisazo-dyestuffs obtainable from the initial components A, the middle components B and C and the end components D:

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	A →	B →	C →	D	Fint of cupriferous dyestuff on cotton
1					reddish grey
2					grey green
3	"				greenish grey
4		"			blackish grey
5		"			grey
6			"		blue green

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EXAMPLE 7.

A dyebath is prepared which contains in 3000 parts of water 0.5 part of the cupriferous dyestuff obtainable as described in Example 1 and 30 parts of crystalline sodium sulphate. 100 parts of cotton are entered into the dye-bath at 50° C., the temperature is raised to 95° C., and dyeing is carried on for one hour

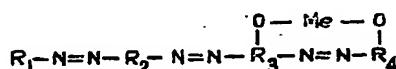
at 90—95° C. The cotton is then rinsed and dried. It is dyed a level greenish grey tint, and the dyeing is distinguished by a very good fastness to light.

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What we claim is:

1. Metalliferous trisazo-dyestuffs which correspond to the formula

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in which the group O—Me—O is bound to the residues R_3 and R_4 in positions vicinal to the azo linkage, Me represents the metal copper or nickel, R_1 represents the residue of an initial component free from hydroxyl groups, R_2 represents an aromatic residue containing at most 10 aryl carbon atoms, R_3 represents an aromatic residue of the benzene series, and R_4 represents a naphthalene residue free from amino groups and containing at least one sulphonic acid group or represents a 5-pyrazolone residue, and in which the azo linkages connected to the residues R_2 and R_3 are bound in para-position relatively to one another.

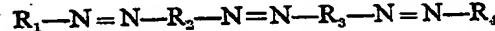
2. Metalliferous trisazo-dyestuffs as claimed in claim 1, which contain at least three and at most six sulphonic acid groups.

3. Metalliferous trisazo-dyestuffs as claimed in claim 2 which contain three or four sulphonic acid groups.

4. Metalliferous trisazo-dyestuffs as claimed in claim 1, 2 or 3, in which the naphthalene residue R_4 contains one or two sulphonic acid groups as the sole further substituents apart from the azo linkage and the —O—Me—O— group.

5. Any one of the metalliferous trisazo-dyestuffs described in Examples 1—6 and in the Table herein.

6. A process for the manufacture of metalliferous trisazo-dyestuffs, wherein a trisazo-dyestuff which corresponds to the general formula



in which R_1 represents the residue of an initial component free from hydroxyl groups, R_2 represents an aromatic residue containing at most 10 aryl carbon atoms, R_3 represents an aromatic residue of the benzene series, and R_4 represents the residue of an oxynaphthalene sulphonic acid free from amino

groups and bound to the azo linkage in a position vicinal to a hydroxyl group or represents a 5-pyrazolone residue, and

R_3 are bound in para-position relatively to one another, and the residue R_3 contains an alkoxy group of low molecular weight in a position vicinal to the azo linkage connecting R_3 with R_4 .

is treated with an agent yielding copper or nickel under conditions such that the corresponding ortho:ortho'-dioxy-azo-metal complex is formed.

7. A process as claimed in claim 6, wherein there is used as starting material a trisazo-dyestuff which contains at least three and at most six, and advantageously three or four, sulphonic acid groups.

8. A process as claimed in claim 6 or 7, wherein there is used as starting material a trisazo-dyestuff in which the residue R_3 represents a benzene residue which contains a methoxy group in ortho-position to the azo linkage connecting R_3 with R_4 .

9. A process as claimed in claim 6, 7 or 8, wherein there is used as starting material a trisazo-dyestuff in which the residue R_4 represents the residue of a monoxy-naphthalene mono- or di-sulphonic acid free from further substituents.

10. A process as claimed in any of claims 6—9, wherein there is used as the agent yielding metal a copper-amine compound.

11. A process for the manufacture of a metalliferous trisazo-dyestuff conducted substantially as described in any one of Examples 1—6 or with reference to the Table herein.

12. A dyeing or printing process in which a metalliferous trisazo-dyestuff claimed in any one of claims 1—5 is used.

13. A dyeing process conducted substantially as described in Example 7.

14. Material which has been dyed or printed by the process claimed in claim 12 or 13.

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